

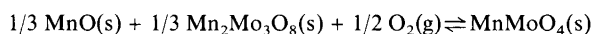
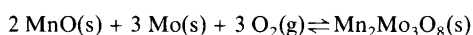
Gibbs Energies of Formation of $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 in the Temperature Range 1100–1400 K

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To determine the thermodynamic stabilities of the intermediate phases $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 , the following redox equilibria were considered:



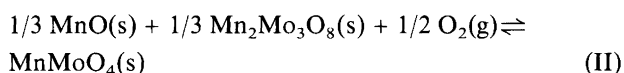
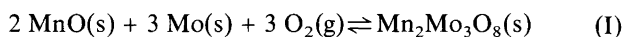
The equilibrium oxygen pressures (p_{O_2}), generated in the temperature range 1100–1400 K, were determined by means of the solid-state EMF technique involving calcia-stabilized zirconia as electrolyte material. The results obtained were used to calculate the standard Gibbs energies of formation ($\Delta_f G^\circ$) for the phases $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 . The stability conditions of these intermediate phases, at 1200 K, are indicated in a diagram with $\lg p_{\text{O}_2}$ and the molar ratio $\text{Mo}/(\text{Mn} + \text{Mo})$ as axes.

Work has progressed for some years at our department in investigating metal–molybdate systems. Thus, Pejryd^{1,2} studied the system Ni–Mo–O, Lindblom^{3–5} the systems SrO–Mo–O and CaO–Mo–O and Rosén and Saitton⁶ the system MgO–Mo–O. These studies include the determination of redox equilibria and thermochemical data for intermediate phases from solid-state EMF measurements. The present study, dealing with the system MnO–Mo–O, forms a continuation of this work.

In the MnO–Mo–O system, two ternary intermediate phases are formed, viz. $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 , that are structurally well characterized.^{7,8} Concerning their thermochemical data at high temperatures, there are only a few previous determinations: Wiesner *et al.*⁹ studied the decomposition of MnMoO_4 and $\text{Mn}_2\text{Mo}_3\text{O}_8$ by thermogravimetric measurements in a controlled atmosphere; Fechter and Oppermann¹⁰ performed solid-state EMF measurements using a tablet arrangement of the electrolyte, the sample and the reference mixtures; and Glathe *et al.*¹¹ carried out solid-state EMF measurements using separated electrode compartments. However, on comparison of the results obtained by the various groups, it is apparent that they differ markedly, and thus a re-determination seemed warranted.

In the temperature range 1100–1400 K the phase relations in the system MnO–Mo–MoO₃ are completely analogous to those indicated in the MgO–Mo–MoO₃

system.⁶ Thus, the following redox equilibria can be established:



In the present work, the oxygen pressures p_{O_2} , generated in accordance with equilibria (I) and (II), have been determined by the solid-state galvanic cell method, which when applied properly can provide high-quality basic data.

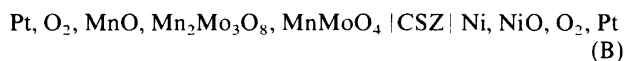
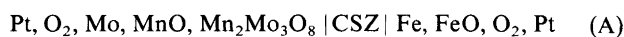
Experimental

Chemicals. The metals Mo (Aldrich, analytical grade), Mn (Riedel *electrolytique*), Fe (Merck *p.a.*), Ni (Merck *p.a.*) and the oxides MoO₂ (Pfalz and Bauer), Fe₂O₃ (Fisher certified) and Mn₂O₃ were all dried before use, usually at about 500 K. All the dried chemicals were stored in a desiccator over silica gel. The metal oxide NiO was synthesized by decomposing basic nickel(II) carbonate (Fluka *p.a.*) at 1200 K. The phases 'FeO' and MnO were prepared by mixing and grinding appropriate amounts of Fe(or Mn) and Fe₂O₃(or Mn₂O₃). The mixtures were then heated at 1273 K for 24 h in a 600 mm long, closed-end Al₂O₃ tube (ampoule). Before heating, the ampoule was evacuated and sealed.

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The intermediate phase $\text{Mn}_2\text{Mo}_3\text{O}_8$ was prepared by heating proper amounts of MnO and MoO_2 in an evacuated ampoule at 1350 K for about 100 h with one intermediate grinding, and the intermediate phase MnMoO_4 by heating MnO_2 and MoO_2 (in a molar ratio 1:1) at 900 K for about 150 h with one intermediate grinding. X-Ray powder diffraction data for the intermediate phases were determined using a Rigaku D/MAX IIA diffractometer, and were in good agreement with corresponding data given in the literature.^{7,8} The following cell parameters were calculated from the present data: MnMoO_4 (monoclinic unit cell, Å), $a = 10.465(2)$, $b = 9.515(2)$, $c = 7.136(1)$, $\beta = 106.18(1)^\circ$; $\text{Mn}_2\text{Mo}_3\text{O}_8$ (hexagonal unit cell, Å), $a = 5.794(1)$, $c = 10.235(1)$.

Galvanic cells used and cell operation. To determine the oxygen pressures, the following oxygen concentration cells, involving calcia-stabilized zirconia (CSZ) as solid electrolyte, were used:



The construction of the galvanic cells is schematically shown in Fig. 1. The closed-end CSZ electrolyte tubes, commercially available from Friedrichsfeld, are 600 mm long with an inner diameter of 5 mm. The sample mixture was kept inside the CSZ tube while the reference system was kept outside in an Al_2O_3 tube (Fig. 1). The electrodes consisted of Pt wires, the inside electrode wound around

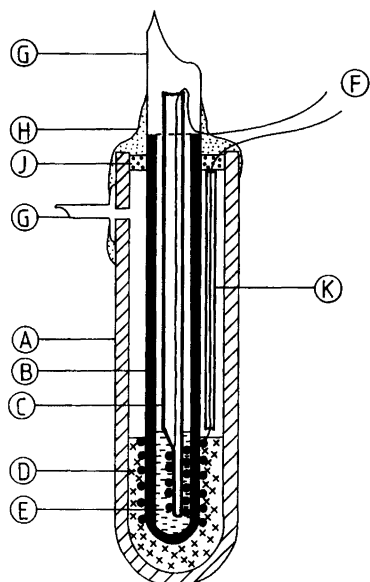


Fig. 1. Sketch of the EMF cell assembly (not drawn to scale). A, Al_2O_3 tube; B, CSZ tube; C, twin-bored Al_2O_3 capillary; D, reference mixture; E, sample mixture; F, Pt-wires; G, sealed pyrex tubes; H, epoxy glue; J, Teflon tape; K, thin Al_2O_3 tube.

the lower end of a Al_2O_3 capillary and the outer one on the outside of the lower tip of the CSZ tube. The cells were heated in a vertical furnace, with non-inductively wound Kanthal A-1 as resistance wire, containing a 30 mm long zone where a uniform temperature was maintained within 1 K. The temperatures of the cells were measured with a Pt/Pt(10 mass % Rh) thermocouple. Both cell and temperature EMFs were recorded via an automatic measuring system involving a high-impedance ($10^{10} \Omega$) digital voltmeter (Solartron 7062).

In a typical run, a cell was initially heated for ca. 24 h at about 1200 K. The temperature was then changed in steps of 20–50 K between the readings. The time between a temperature change and taking a data point was 5–50 h, depending on the temperature level. To establish that equilibrium values were achieved, the EMF measurements were carried out by both increasing and decreasing the cell temperatures. After a run, all sample mixtures were checked and verified by X-ray powder diffraction.

Results and calculations

EMF values obtained. A number of measuring points (E_{exp}/mV , T/K) were determined with the cell configurations (A) and (B). Values obtained are given in Tables 1 and 2. For each cell, values were obtained from two runs, where each run started with a newly assembled cell charged with 'fresh' chemical mixtures. The measured values, 61 data points with cell (A) and 26 points with cell (B), were smoothed by a least-squares treatment to evaluate the following $E(T)$ relationships (the T -values are assumed to be exact):

$$E(\text{A})/\text{mV} = 73.98 + 0.63750(T/\text{K}) - 0.21373(T/\text{K}) \lg(T/\text{K}) \quad (1)$$

$$(1090 \leq T/\text{K} \leq 1355)$$

$$E(\text{B})/\text{mV} = -42.10 - 1.0548(T/\text{K}) + 0.36010(T/\text{K}) \lg(T/\text{K}) \quad (2)$$

$$(1100 \leq T/\text{K} \leq 1365)$$

Calculated standard deviations of the fit are: $\sigma E(\text{A}) = \pm 0.42 \text{ mV}$ and $\sigma E(\text{B}) = \pm 0.71 \text{ mV}$. Relationships (1) and (2) correspond to the assumption of a constant (but non-zero) value of ΔC_p for the equilibrium reactions considered. Calculated values of the deviations $\Delta E = E_{\text{exp}} - E$ are also given in Tables 1 and 2.

Calculation of oxygen pressures. The equilibrium oxygen pressures of the equilibria studies [$p_{\text{O}_2}(\text{I})/\text{bar}$ and $p_{\text{O}_2}(\text{II})/\text{bar}$] are related to the EMF (E/mV) and temperature (T/K) values and the reference oxygen pressures ($p_{\text{O}_2}^*/\text{bar}$) by the equations

$$\lg[p_{\text{O}_2}(\text{I})/\text{bar}] = \lg[p_{\text{O}_2}^*(\text{Fe/FeO})/\text{bar}] - 4F/(R \ln 10)E(\text{A})/(T/\text{K}) \quad (3)$$

Table 1. Basic experimental data, E_{exp}/mV and T/K , and calculated values, $\Delta E = E_{\text{exp}} - E(\text{A})$, obtained for cell (A).

T/K^a	E_{exp}	$E_{\text{exp}} - E(\text{A})$	T/K	E_{exp}	$E_{\text{exp}} - E(\text{A})$
1087.5	60.75	-0.76	1244.5	43.80	-0.33
1100.8	60.22	0.11	1245.0	44.19	0.12
1108.4	60.03	0.72	1246.0	43.82	-0.13
1110.9	59.11	0.07	1251.3	42.08	-1.25
1113.6	58.26	-0.50	1255.3	43.01	0.15
1121.0	58.08	0.11	1262.0	42.33	0.26
1124.7	57.12	-0.45	1265.0	42.08	0.36
1131.4	57.13	0.28	1266.8	41.34	-0.17
1134.9	57.10	0.63	1271.0	40.79	-0.22
1139.4	55.45	-0.53	1271.6	41.30	0.36
1147.3	55.14	0.02	1276.7	39.27	-0.11
1150.6	55.35	0.59	1281.7	39.87	0.14
1160.3	54.08	0.39	1281.8	39.22	-0.50
1162.7	53.66	0.23	1287.4	38.99	-0.06
1165.7	52.55	-0.55	1290.9	39.06	0.43
1173.3	52.19	-0.06	1297.2	37.91	0.04
1176.5	52.33	0.43	1298.4	38.13	0.40
1183.3	51.34	0.20	1308.1	36.72	0.17
1186.9	50.82	0.09	1308.2	36.65	0.11
1192.1	49.57	-0.58	1313.5	35.28	-0.62
1192.7	50.14	0.06	1316.8	36.01	0.52
1199.3	49.13	-0.20	1323.0	35.23	0.50
1202.5	49.32	0.35	1324.1	34.82	0.22
1209.8	47.94	-0.20	1328.9	34.17	0.16
1212.8	48.03	0.24	1334.7	33.01	-0.29
1218.1	46.78	-0.41	1339.3	32.78	0.05
1219.3	47.19	0.14	1340.0	32.09	-0.55
1225.3	46.19	-0.17	1349.7	32.07	0.63
1229.0	46.14	0.21	1351.0	30.97	-0.31
1235.9	45.25	0.12	1354.9	30.68	-0.11
1239.3	45.11	0.37			

^aTemperature values in italics correspond to a series of increasing temperatures.

$$\lg[p_{\text{O}_2}(\text{II})/\text{bar}] =$$

$$\lg[p_{\text{O}_2}^*(\text{Ni/NiO})/\text{bar}] - 4F/(R \ln 10)E(\text{B})/(T/\text{K}) \quad (4)$$

where R is the gas constant ($8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$), F the Faraday constant ($96484.56 \text{ C mol}^{-1}$), \lg denotes base-10 logarithms and $1 \text{ bar} = 10^5 \text{ Pa}$. The reference oxygen pressures ($p_{\text{O}_2}^*/\text{bar}$) can be expressed by the equations^{12,13}

$$\lg[p_{\text{O}_2}^*(\text{Fe/FeO})/\text{bar}] = -0.8839 - 26506/(T/\text{K}) + 2.2012 \lg(T/\text{K}) \quad (5)$$

$$\lg[p_{\text{O}_2}^*(\text{Ni/NiO})/\text{bar}] = 8.055 - 24274/(T/\text{K}) + 0.22657 \lg(T/\text{K}) \quad (6)$$

the uncertainty in $\lg[p_{\text{O}_2}^*/\text{bar}]$ being ± 0.004 and ± 0.009 , respectively, at 1300 K . By combining eqns. (1), (3) and (5), and (2), (4) and (6), the following equations can be derived:

$$\lg[p_{\text{O}_2}(\text{I})/\text{bar}] = -13.74 - 27997/(T/\text{K}) + 6.5098 \lg(T/\text{K}) \quad (7)$$

$$(1090 \leq T/\text{K} \leq 1360; \quad \delta \lg[p_{\text{O}_2}(\text{I})/\text{bar}] = \pm 0.007)$$

$$\lg[p_{\text{O}_2}(\text{II})/\text{bar}] = 29.32 - 23425/(T/\text{K}) - 7.0328 \lg(T/\text{K}) \quad (8)$$

$$(1100 \leq T/\text{K} \leq 1365; \quad \delta \lg[p_{\text{O}_2}(\text{II})/\text{bar}] = \pm 0.012)$$

Calculation of ΔG° -values. The Gibbs energies (ΔG°) for the various equilibria can be evaluated from the general expression

$$\Delta G^\circ/\text{J} = -R \ln 10 T \lg K$$

where the equilibrium constant K can be substituted as follows:

$$\lg K(\text{I}) = -3 \lg[p_{\text{O}_2}(\text{I})/\text{bar}] \quad (9)$$

$$\lg K(\text{II}) = -1/2 \lg[p_{\text{O}_2}(\text{II})/\text{bar}] \quad (10)$$

Using eqns. (7)–(10) the following relationships are derived:

$$\Delta G^\circ(\text{I})/\text{J} = -1607980 - 789.14(T/\text{K}) + 373.88(T/\text{K})\lg(T/\text{K}) \quad (11)$$

$$(1090 \leq T/\text{K} \leq 1355; \quad \delta \Delta G^\circ(\text{I})/\text{J} = \pm 500)$$

$$\Delta G^\circ(\text{II})/\text{J} = -224230 + 280.66(T/\text{K}) - 67.320(T/\text{K})\lg(T/\text{K}) \quad (12)$$

$$(1100 \leq T/\text{K} \leq 1365; \quad \delta \Delta G^\circ(\text{II})/\text{J} = \pm 150)$$

From equilibria (I) and (II) the Gibbs energies of formation of $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 are derived accordingly:

$$\Delta_f G^\circ(\text{Mn}_2\text{Mo}_3\text{O}_8) = \Delta G^\circ(\text{I}) + 2\Delta_f G^\circ(\text{MnO}) \quad (13)$$

$$\Delta_f G^\circ(\text{MnMoO}_4) = \Delta G^\circ(\text{II}) + 1/3\Delta_f G^\circ(\text{MnO}) + 1/3\Delta_f G^\circ(\text{Mn}_2\text{Mo}_3\text{O}_8) \quad (14)$$

In the temperature range considered, the following $\Delta_f G^\circ(T)$ relationship for MnO was derived, using data from Alcock:¹⁴

$$\Delta_f G^\circ(\text{MnO})/\text{J mol}^{-1} = -388490 + 76.24(T/\text{K}); \quad (\pm 600 \text{ J}) \quad (15)$$

Using eqns. (11)–(15) the following relationships can be calculated:

$$\Delta_f G^\circ(\text{Mn}_2\text{Mo}_3\text{O}_8)/\text{J mol}^{-1} = -2384960 - 636.66(T/\text{K}) + 373.88(T/\text{K})\lg(T/\text{K}) \quad (16)$$

$$(1090 \leq T/\text{K} \leq 1360; \quad \delta \Delta_f G^\circ/\text{J mol}^{-1} = \pm 1500)$$

$$\Delta_f G^\circ(\text{MnMoO}_4)/\text{J mol}^{-1} = -1148720 + 93.853(T/\text{K}) + 57.307(T/\text{K})\lg(T/\text{K}) \quad (17)$$

$$(1100 \leq T/\text{K} \leq 1360; \quad \delta \Delta_f G^\circ/\text{J mol}^{-1} = \pm 700)$$

Discussion

To assess the present data, the results given in the two earlier solid-state EMF studies^{10,11} are judged to be more dependable than those from the thermogravimetric mea-

Table 2. Basic experimental data, E_{exp}/mV and T/K , and calculated values, $\Delta E = E(B)$, obtained for cell (B).

T/K^a	E_{exp}	$E_{\text{exp}} - E(B)$	T/K	E_{exp}	$E_{\text{exp}} - E(B)$
1097.4	2.04	0.20	1270.5	39.33	1.46
1123.9	7.36	0.27	1270.9	38.33	0.37
1134.2	8.73	-0.43	1281.5	40.26	-0.03
1150.4	12.48	0.04	1283.5	39.65	-1.08
1160.9	14.34	-0.25	1297.1	43.98	0.23
1176.4	18.00	0.21	1307.7	45.71	-0.40
1187.6	18.93	-1.19	1309.4	45.81	-0.68
1192.7	21.52	0.33	1323.3	49.91	0.29
1213.6	25.64	0.05	1334.0	51.83	-0.21
1229.2	28.92	0.00	1336.8	50.98	-1.70
1244.7	32.61	0.36	1349.7	55.40	0.22
1255.4	34.66	0.09	1360.3	58.93	0.88
1256.1	35.45	0.73	1364.0	59.56	0.66

^aTemperature values in italics correspond to a series of increasing temperatures.

surements.⁹ Considering the two EMF studies, different electrolyte arrangements were utilized. Fechter and Oppermann¹⁰ had the electrolyte in the form of a tablet placed between the sample and the reference mixtures pressed to tablets, while Glathe *et al.*¹¹ separated the solid mixtures using an electrolyte tube. In the former cell construction, the sample and reference mixtures are in contact with the same gas phase, and oxygen can diffuse from one side of the tablet to the other. This undesirable diffusion is avoided through the tube construction and the results obtained by Glathe *et al.*¹¹ should, therefore, be more reliable than those from the tablet arrangement. On comparison, the values given by Glathe *et al.*¹¹ are in fact quite close to those obtained in the present study. By way of example, eqns. (11) and (12) give the following values at 1300 K (in kJ): $\Delta G^\circ(\text{I}) = -1120.3 \pm 0.5$ and $\Delta G^\circ(\text{II}) = -131.9 \pm 0.2$. Corresponding ΔG° -values given by Glathe *et al.*¹¹ are: -1124.3 ± 2 and -134.0 ± 0.4 , respectively. It therefore seems fair to claim that the $\Delta_f G^\circ$ -values evaluated in the present study for $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 , given by eqns. (16) and (17), can be considered as the most reliable, available at present.

Figure 2 summarizes the present results concerning the stability conditions of the intermediate phases $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 at 1200 K. This diagram is constructed with $\lg[p_{\text{O}_2}/\text{bar}]$ and the molar ratio $\text{Mo}/(\text{Mn} + \text{Mo})$ as axes. The phase boundaries between the pairs Mo/MoO_2 and $\text{MnO}/\text{Mn}_3\text{O}_4$ are obtained using data given by Pejryd¹ and by Huang and Rosén¹⁵, respectively. As can be seen from the diagram, there is a two-phase region with both the intermediate phases present, but only in a rather limited range of conditions.

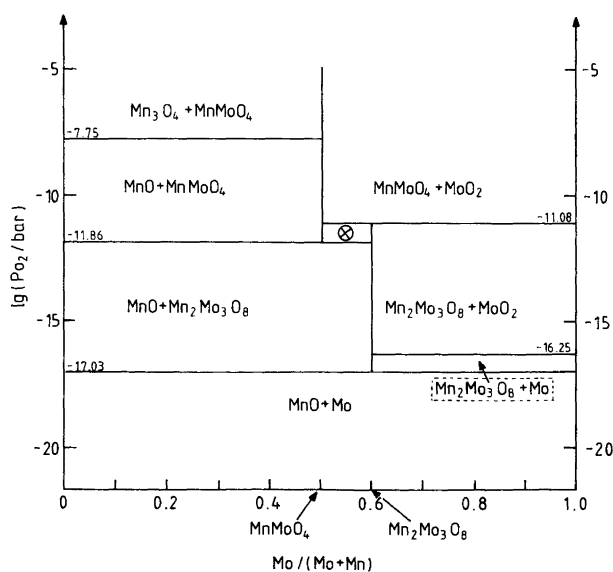


Fig. 2. Diagram of $\lg[p_{\text{O}_2}/\text{bar}]$ as a function of the molar ratio $\text{Mo}/(\text{Mn} + \text{Mo})$, showing the stability ranges of the intermediate phases $\text{Mn}_2\text{Mo}_3\text{O}_8$ and MnMoO_4 at 1200 K. In the range marked with the symbol \otimes , the two intermediate phases coexist.

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